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Application of Solid-State and High-Pressure Reactions for Fullerene Derivatization and CO₂ Activation (ORGANIC MATERIALS CHEMISTRY-High-Pressure Organic Chemistry)

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Application of Solid-State and High-Pressure Reactions for Fullerene Derivatization and CO₂ Activation

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Under the solid-state reaction conditions, a nucleophilic addition of organozinc reagent occurs on fullerene C₆₀ to give a monoadduct together with a bisadduct and a cyclopropanofullerene. Surprisingly, the fullerene C₆₀ also undergoes a clean [2+2] type dimerization by the action of KCN or Mg powder under the similar reaction conditions. The fullerene dimer thus obtained is the very first example of (C₆₀)₂, and its structure has been determined by the X-ray crystallography. The use of high pressure (5000 atm) was also shown to be advantageous for a liquid-phase [4+2] cycloaddition of C₆₀. The high-pressure reaction of CO with supercritical CO₂ has been found to effect the C-C bond formation affording an oxalate salt in good yield in the presence of Cs₂CO₃.

Keywords: C₆₀ / solid-state-reaction / cyclodimerization / organozinc reagent / supercritical CO₂ / CO

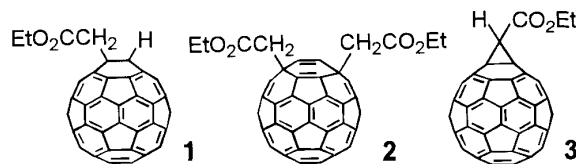
The use of extraordinary reaction conditions can sometimes bring about unique results which are hardly attainable by other methods. Here we report typical such examples recently obtained in our research group.

(1) A Solid-State Reformatsky-type Reaction of Fullerene C₆₀ [1].

The chemical functionalization of fullerene C₆₀ has been the subject of intensive research both from the academic standpoint and for exploring the applicability of this new carbon allotrope as functional materials. However, the researchers are often confronted with the extremely low solubility of C₆₀ in common organic solvents. In order to circumvent such difficulty, we explored a novel method of

reacting C₆₀ with nucleophiles without any solvent.

As a typical example of Reformatsky-type reaction, a mixture of C₆₀, Zn powder, and ethyl bromoacetate (in a molar ratio of 1:20:5) was placed in a stainless-steel capsule of a vibrating mixer containing a stainless-steel mixing ball under nitrogen. The mixture was vigorously agitated for 20 min at room temperature, treated with toluene-CF₃CO₂H, and separated by chromatography to give adduct 1 in 63% yield



ORGANIC MATERIALS CHEMISTRY —High-Pressure Organic Chemistry—

Scope of Research

Fundamental studies are being made for creation of new functional materials with novel structures and properties and for utilization of high pressure in organic synthesis. The major subjects are: synthetic and structural studies on novel cyclic π -systems; chemical transformation of fullerene C₆₀; utilization of carbon monoxide and dioxide for organic synthesis under the transition-metal catalysis.



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based on consumed C_{60} together with minor products **2** and **3**. All the products were fully characterized by 1H and ^{13}C NMR, IR, UV-vis, and MS spectra.

Preliminary experiments showed that a Grignard reagent can be prepared and can react with C_{60} under similar conditions.

(2) The First Synthesis of Fullerene Dimer (C_{60})₂ [2].

The all-carbon fullerene polymers are quite promising as new carbon materials. However, there has so far been absolutely no experimental evidence for the all-carbon fullerene dimer, which should be an important structural unit of these polymers.

When we conducted the solid state reaction of C_{60} with KCN under the similar conditions as above, new C_{60} dimer **4** was isolated for the first time, in 60% yield based on consumed C_{60} , instead of a cyano derivative. The same dimer was similarly obtained by the reaction of C_{60} with magnesium powder albeit in a lower yield (6%).

Dimer **4** is a dark brown crystal, which is hardly soluble in most of the organic solvents except *o*-dichlorobenzene (ODCB). The structure of **4** was assigned first based on the ^{13}C NMR spectrum exhibiting 16 signals in the sp^2 -carbon region and one signal (δ 76.22) in the sp^3 -carbon region, and on the UV-vis spectrum (λ_{max} 328, 434, and 698 nm).

The structure was decisively determined by X-ray crystallography for a single crystal grown from ODCB. As shown in Figure 1, dimer **4** is composed of two C_{60} cages sharing a cyclobutane ring.

Reflecting the elongation of the linking bond between two C_{60} cores (1.575(7) Å), dimer **4** readily dissociates into two C_{60} molecules by heating at 175 °C for 15 min. This dissociation was also observed upon electrochemical reduction as examined by cyclic voltammetry and differential pulse voltammetry. This facile formation of **4** will open up the way to the fundamental study on the nature of fullerene polymers.

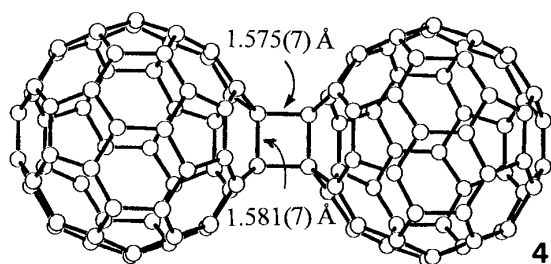
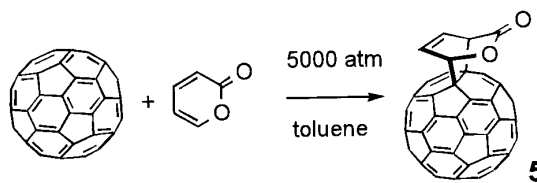


Figure 1. X-Ray crystal structure of the first fullerene dimer **4**. The crystallography was conducted by Dr. Motoo Shiro of Rigaku Corp.

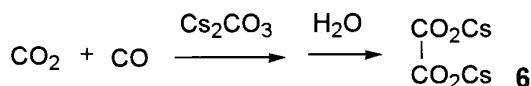
Another reaction under extraordinary conditions, i.e. a liquid-phase high-pressure reaction (5000 atm), was also found to be advantageous for cycloaddition of C_{60} leading to the adduct such as **5** [3].



(3) Novel C-C Bond Formation between CO and Supercritical CO₂ in the Presence of Cs₂CO₃.

The efficient utilization of carbon dioxide is one of the most important issues of today, both from the chemical and environmental viewpoints. We found that a reaction of pressurized CO with CO₂ affords oxalate salt **6** in high yield in supercritical CO₂ in the presence of Cs₂CO₃.

As a typical example, **6** was obtained in 90% yield (based on charged Cs₂CO₃) after the reaction for 2 h at 380 °C under 50 atm of CO and 110 atm of CO₂ (0.28 mol) in the presence of Cs₂CO₃ (4.5 mmol) in a glass-lined autoclave (20 ml) with shaking.



Based on results of various control experiments including ^{13}C labeling, it was unambiguously proven that the present C-C formation occurs by way of the reductive capture of CO₂ with CO in which Cs₂CO₃ is playing a crucial role [4].

On the other hand, the action of methanol in place of CO under the similar reaction conditions as above effected the formation of HCO₂Cs (135%), H₂ (715%), and CO (463%), thus demonstrating further applicability of supercritical carbon dioxide.

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